Functional evaluation of compatibilization systems for recycled PP-PET blends

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ABSTRACT: The main goal of this study is to investigate the effect of different compatibilizers on mechanical properties in blends of polypropylene (PP) and poly(ethylene terephthalate) (PET). The blends have been prepared by twin screw extrusion followed by injection molding at a weight ratio of 80/20. The compatibilizers, PP grafted with maleic anhydride (PP-g-MA), polyolefin based elastomer grafted with MA (POE-g-MA), poly[styrene-b-(ethylene-co-butylene)-b-styrene] grafted MA (SEBS-g-MA), SEBS grafted glycidyl methacrylate (SEBS-g-GMA) and non-functionalized SEBS were added in a fixed weight percentage. Their effect on the mechanical performances of the blend was measured using tensile, flexural and impact tests. These tests revealed that, for this specific blend, improving the impact properties is most successful with POE-g-MA, while PP-g-MA performs better at improving the tensile and flexural properties. In comparison to the polyolefin-based compatibilizers, the SEBS-based compatibilizers displayed little or even a negative effect on the mechanical properties of the PP/PET blends.

1 INTRODUCTION

Today, the plastic waste disposal represents one of the biggest challenges for the environment. There is a great amount of plastic waste, which mostly comes from packaging applications, as many of these plastic products are not designed for long-term usage. One of the ways of reducing landfilling is by mechanically recycling these waste streams. Often, polypropylene (PP) and poly(ethylene terephthalate) (PET) are found in these packaging products but are very hard to separate. This implies that a lot of recycled plastic waste comes as a mixture of different types of plastics. As known, many polymers are immiscible in the melt phase, causing distinct phase morphologies and poor mechanical properties in the final recycled products. Hence, there are intensive studies of researchers on the development of new methods, which could overcome the immiscibility of polymer waste and by this improve the final product performance (Pek & Ghosh 2015; Kuzmanović et al. 2016; Asgari & Masoomi 2012; Ragaert et al. 2017; Chiu & Hsiao 2006). In order to mitigate the disadvantages of immiscibility, compatibilization is known as a promising method to improve the compatibility of PP/PET blends (Asgari & Masoomi 2012; Chiu & Hsiao 2006; Heino et al. 1997; Jayanarayanan et al. 2015; Champagne et al. 1999; Zhu et al. 2015; Evstatiev et al. 2005). Conventional compatibilizers are polyolefins or rubber based polymers grafted with reactive functional groups, such as acrylic acid (AA), maleic anhydride (MA) or glycidyl methacrylate (GMA) (Jayanarayanan et al. 2015). The compatibilization of the blends can have a substantial influence on the interfacial properties between phases as the compatibilizer concentrates itself at the interface between the different phases during blending, preventing coalescence and resulting in smaller and finer dispersions as well as a better adhesion between the polymer phases (Zhang et al. 2009; Entezam et al. 2012; Pang et al. 2000). Many researchers reported that PP grafted with maleic anhydride (PP-g-MA) could improve the compatibility of PP/PET blends. Heino et al. (Heino et al. 1997) found that poly[styrene-b-(ethylene-co-butylene)-b-styrene] (SEBS) grafted with MA or GMA could act as a compatibilizer to yield a finer dispersion by improving the interfacial adhesion in the mixture PET/PP. Ample studies reported results on the effect of adding different amounts of compatibilizers.

This research focuses on adding different compatibilizers with a fixed weight percentage. A variety of compatibilizers exist for improvement of blend properties and in this article an extensive study on the comparison of the effectiveness of five different compatibilizers in the PP/PET blend is reported: PP-g-MA, polyolefin based elastomer grafted with MA (POE-g-MA), SEBS, SEBS-g-MA and SEBS-g-GMA. In this regard, the mechanical properties in terms of tensile, flexural and impact testing are investigated and compared to the virgin blend in order to determine the influence of the compatibilizers.

2 MATERIALS AND METHODS

2.1 *Materials*

The PP was kindly donated by ExxonMobil (PP6272NE1) with a melt flow rate (MFR) of 2.8 g/10 min (2.16 kg, 230 ºC), and the used PET was LIGHTER C93 from Equipolymers, which is a bottle-grade material with an intrinsic viscosity of 0.80 ± 0.02 dL/g. PET was dried in a vacuum oven for 24 h at 80 ºC before processing, while PP was used as received. Five different compatibilizers were used in this research. PP-g-MA (SCONA TPPP 2003 GB) and SEBS-g-GMA (SCONA TPKD 8304 PCC) were kindly donated by BYK Additives & Instruments. The POE-g-MA used was Acti-Tech 16MA13, kindly donated by Nordic Grafting Company (NGC). SEBS-g-MA (FG1901 G) and SEBS (G1657M) were kindly donated by Kraton. The reported grafting percentages of the functional groups are listed in Table 1. All compatibilizers were dried at 80 ºC for 24 h before processing.

Table 1: Grafting percentage of MA and GMA functional groups in compatibilizers. Data in table was found in technical data sheets, provided by the supplier

Material	Grafting percentage [wt%]
PP-g-MA	0.9-1.3
SEBS-g-GMA	3.5
POE-g-MA	1.3
SEBS-g-MA	1.4
SEBS	0

2.2 *Sample preparation*

The polymers were mixed in a weight ratio of 80/20 PP/PET and compatibilizers were added in 6 wt%, while maintaining the same PP to PET ratio. Blends were prepared by extrusion followed by injection moulding. The PP and dried PET pellets, as well as dried compatibilizer were dry mixed in the correct weight ratio before being melt mixed. The melt mixing of the polymers (with and without compatibilizer) was done using a twin-screw extruder (Coperion ZSK18) with two co-rotating screws of 18 mm diameter. The rotation speed of the screw was set at 120 rpm, while the temperature profile was fixed at 205 °C, 245 °C, 250 °C, 250 °C, 255 °C, 255 °C, 260 °C, 260 °C, 260 °C, from hopper to die. The extrudate was obtained as a sheet with dimensions of 25x1 mm. The next step consisted of shredding the sheets, followed by injection moulding with an Engel 80T using a temperature profile of 180 °C, 190 °C, 200 °C and 210 °C in a standard mould with a temperature of 30 °C, obtaining both ISO 527 tensile and ISO 178 impact and flexural bars.

2.3 *Characterization*

All mechanical characterization was conducted under controlled conditions, being at 23 ºC and 50% humidity, after letting the samples rest for a minimum of 48 hours within this controlled environment.

The notched Charpy impact test was used to evaluate the toughness of the samples. The impact bars were analyzed by using the Tinius Olsen IT 503 Pendulum Impact Tester according to ISO 179.The specimens were notched in the middle of the sample with a depth of 2 mm and then placed horizontally with the notch oriented away from the pendulum with energy of 2 J. At least 10 measurements were done for each sample.

The standard tensile bars were tested with an Instron 5565 tensile device according to ISO 527. During the tests, different test speeds were used before and after removing the extensometer (gauge length 12.5 mm), 3 mm/min and 10 mm/min respectively.

The three-point flexural test was performed with an Instron 4464 testing machine (Norwood, MA USA). The test was done according to the ISO 178 standard. The distance between both support spans was set at 48 mm, while the deflection rate was set at 5 mm/min. Analysis was performed using the Bluehill software.

At least 5 specimens were tested during flexural and tensile tests. Results are reported as mean ± standard deviation. Statistical analysis of all specimens was performed by software package SPSS Statistics 23 (Armonk, NY, USA) (t-independent test, $p=0.05$).

3 RESULTS AND DISCUSSION

3.1 *Impact properties*

It is well known that uncompatibilized polymer blends have inferior properties due to immiscibility between the phases (Kuzmanović et al. 2016; Asgari & Masoomi 2012). The goal of this research was to investigate the influence of different compatibilizers on the mechanical properties of a PP/PET blend.

Figure 1 presents impact strength values of the different samples. A significant increase can be seen in toughness for the compatibilized blends PP-g-MA, POE-g-MA and SEBS-g-MA compared to the neat blend, and no significant increase for SEBS-g-GMA and SEBS. The samples containing the POE-g-MA compatibilizer showed the highest value for impact. This could be explained by the fact that POE contains randomly ordered propylene and ethylene blocks in an elastomeric structure compared to PP-g-MA containing only relatively rigid propylene. SEBS based compatibilizers are rubber-like as well but more rigid compared to POE backbones due to the styrene end blocks. POE-g-MA is as such more effective in improving the impact resistance by better dissipation of the impact energy (G'Sell et al. 2004; Wang et al. 2016). In theory, the POE phase could initiate crazes contributing to the dissipation of the impact energy to block the crack propagation

(Wang et al. 2016). PP-g-MA improves the compatibility of both phases as well, resulting in an improved impact strength compared with the non-compatibilized sample by better transferring the stress over the phases. When comparing the influence of the POE-g-MA to the PP-g-MA, the rubber-like backbone seems superior in dissipating energy for impact resistance than the better stress conveying system inherent to the PP-g-MA, this can be seen by a decrease in impact energy (G'Sell et al. 2004). The beneficial effects of the POE backbone are also confirmed by the results of the strain at break in the tensile tests (Table 2), which are considerably higher compared to the more rigid SEBS and PP backbones.

PP-g-MA compatibilized blends show better results compared to blends containing SEBS based compatibilizers because of better compatibility of the PP backbone with the PP matrix. That said, the SEBS-g-MA showed a small increase relative to the other two SEBS based compatibilizers. Here, the polar carboxyl groups of MA grafted onto the compatibilizer's backbone improve adhesion with the PET phase by lowering the interfacial tension. The same interaction can be seen with the PP-g-MA, in which adhesion between the PP and PET phases is improved because of the same backbone structure. Because of this backbone difference, the SEBS-compatibilizers do not benefit the same compatibility, resulting in a decrease in adhesion between the two phases for these blends. This is reflected in the lower impact values of the SEBS-blends where SEBS-g-GMA and SEBS did not show any significant improvement compared to the uncompatibilized sample.

Different researchers have compared the differences between GMA and MA groups, where the GMA functional group was found to be more reactive than MA due to its bifunctional character (Chiu & Hsiao 2006; Heino et al. 1997; Van Bruggen et al. 2016). Nevertheless, the difference in grafting percentage also needs to be taken into account, where the GMA percentage is 3.5wt% in SEBS-g-GMA and 1.4wt% of MA content in SEBS-g-MA. Tanrattanakul et al. (Tanrattanakul et al. 1997) have investigated the effect of different contents of grafted MA in compatibilizers for PET-rich blends and they reported that the increased percentage of grafting groups could have a negative effect such as a decrease in fracture energy. For the current case, it would be interesting to verify the effect of grafting percentage of anhydride for our system, which is a PP-rich blend.

The blend with non-functionalized SEBS displays lower impact strength compared with neat blend PP/PET. Here, the system can be seen as a ternary blend causing a decrease in impact energy. The rubber phase is too low to be effective without grafted functional groups. SEBS itself could still be located

Figure 1: Comparison of impact strengths of the different blends

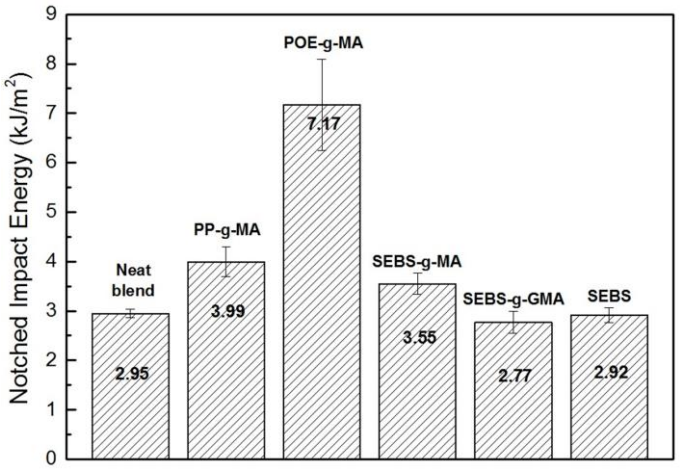


Table 2: Strain at break of the blends

Material	Strain at break (%)
Neat blend	9.83
PP-g-MA	102.16
POE-g-MA	401.07
SEBS-g-MA	13.58
SEBS-g-GMA	7.31
SEBS	13.08

Figure 2: Comparison of the tensile modulus of the different blends

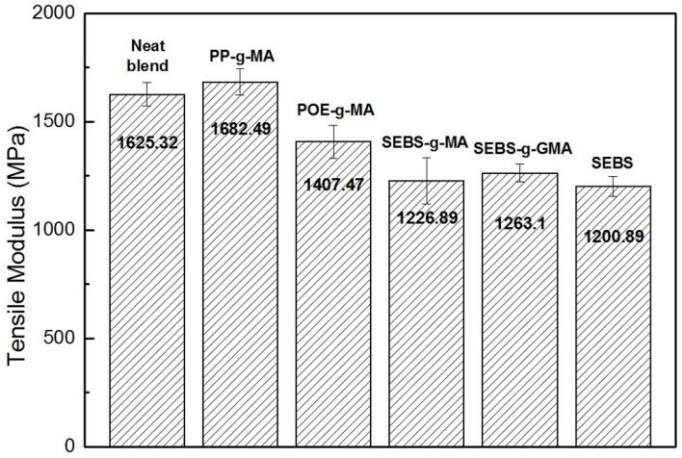
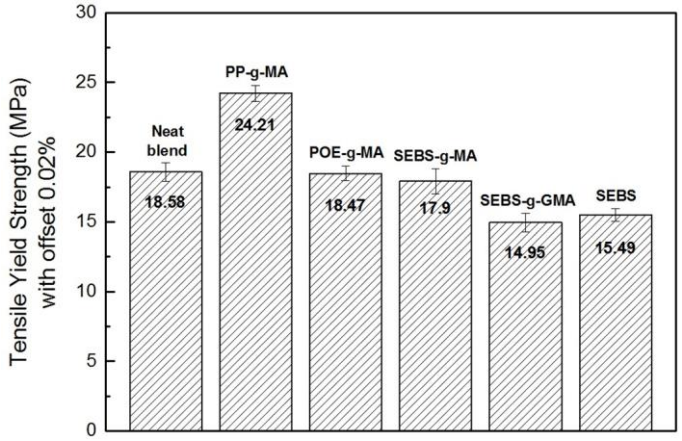


Figure 3: Comparison of tensile strength of the different blends



at the interface and act as a compatibilizer, increasing the physical interactions. Nevertheless, this ternary structure makes it more complicated because it can contain cavities, core-shell and individual particles simultaneously, which do not effectively absorb the impact energy (Heino et al. 1997; Moini Jazani et al. 2015).

3.2 *Tensile and flexural properties*

The tensile modulus and strength for all samples are given in Figure 2 and Figure 3 respectively. The bar graphs show that PP-g-MA is the only compatibilizer succeeding in maintaining the stiffness of the original blend. This can be explained by the higher stiffness of the PP backbone to the other compatibilizers containing softer backbones such as SEBS and POE. PP-g-MA greatly improves the compatibility between PP and PET, reducing the interfacial energy, and forming an interphase layer between the matrix and particles, increasing interfacial bonding. The adhesion is considerably higher when compared to SEBS-g-GMA and POE-g-MA.

Next, the lower adhesion in POE-g-MA also causes a lower tensile strength which can again be explained by the aforementioned presence of elastomeric chains in the polymer backbone which are less compatible with the two phases (G'Sell et al. 2004). G'Sell et al. explained that several mechanisms could contribute to the general deformation of the sample under tension: interface decohesion, cavitation at the PP/PET interface and the cavitation in POE-g-MA particles. Blends with SEBS, SEBS-g-MA and SEBS-g-GMA have shown a slight decrease in modulus compared POE-g-MA and a significant decrease compared to PP-g-MA and neat PP/PET.

Additionally, all tested blends have shown a mostly brittle breakage during the tensile tests, except for PP-g-MA and POE-g-MA where necking was observed. This can also be seen in the results for strain at break represented in Table 2, the values are much higher for the blends containing POE-g-MA when compared to all other blends. This is because of the rubber blocks in the POE-g-MA and the improved compatibility between both phases of the blend. PP-g-MA improves the adhesion as well, but will show a less pronounced strain due to its more rigid backbone. It was observed that non-compatibilized blends show a low elongation at break, due to the low interfacial adhesion between phases. The strain was slightly improved with the addition of SEBS and SEBS-g-MA to the blend, likely because of their rubbery-structure. However, due to their low improvement in compatibility of the PP matrix with the PET this effect is barely noticeable.

Figure 4 and 5 presents the results of the flexural modulus and strength of the tested samples. Depending on the polymer backbones and their functionality existing research (Jayanarayanan et al. 2015) has

Figure 4: Comparison of flexural modulus for the different blends

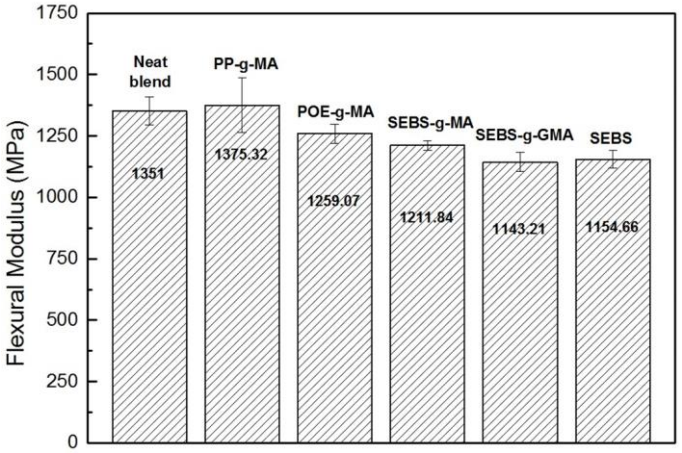
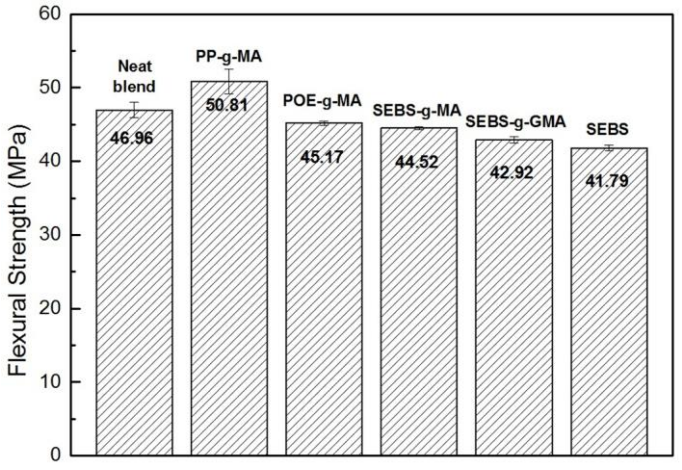


Figure 5: Comparison of flexural strength for the different blends



demonstrated that the addition of a rubber based compatibilizer could lower the values of flexural properties. In this article, the highest flexural modulus and strength is achieved for PP-g-MA blends, which is consistent with the results obtained during the tensile testing. A similar improvement can be noticed in flexural strength compared to other samples. These results indicate that no decohesion between the PP matrix and the PET particles occurs due to improved compatibility. Along with the stiff backbone of PP-g-MA this leads to the improvement of flexural strength. Hence, PP-g-MA displays optimal flexural properties when comparing with other compatibilizers. Further, there are no remarkable differences in flexural modulus and strength between other blends. The lower flexural modulus and strength are caused by the elastomeric nature of POE and SEBS backbones, which are not resistant to the applied flexural force.

4 CONCLUSION

The effect of different compatibilizers on the mechanical properties of blends consisting of a 80/20 ratio PP/PET was studied. The comparison between

different backbones and functional groups was made in this regards. Five different compatibilizers were investigated: PP-g-MA, POE-g-MA, SEBS-g-MA, SEBS-g-GMA and non-functionalized SEBS were used in a fixed percentage being 6 wt%.

The POE-g-MA compatibilizer exhibited a great improvement in impact strength due to the elastomeric nature of its backbone structure and improved compatibility between the PP and PET phases. PP-g-MA showed a slight improvement in impact strength due to its good compatibility with the PP phase because of its PP backbone. In the case of SEBS-g-MA, the slightly enhanced impact strength can be ascribed to the rubber blocks in SEBS backbone. However, it causes a smaller improvement in compatibility compared with PP-g-MA and POE-g-MA. In this regard, the lowest value was obtained by SEBS-g-GMA, i.e. the compatibilizer with the highest grafting percentage of anhydride. This could be the reason for the decrease in impact strength regarding to the literature, nevertheless these assumptions need experimental verification. In the case of SEBS, lower impact strength was observed relative to the neat PP/PET blend which could be ascribed to the formation of ternary blends denoting a complete absence of compatibility between the phases as the rubber content is too low to react effectively without functional groups.

The tensile tests revealed that PP-g-MA improved the tensile modulus and strength the best due to the stiff nature of the backbone, while the other compatibilizers contain rubber-like blocks resulting in a decreased tensile modulus and strength. The same conclusion can be drawn for the flexural properties. The PP-g-MA shows a similar improvement due to good compatibility between the PP chains and the PP backbone of the compatibilizing agents, increasing adhesion between PP and PET. The other compatibilizers have not shown an improvement, due to the content of elastomeric groups. The MA-based compatibilizers (PP-g-MA, POE-g-MA and SEBS-g-MA) generally performed better than the non-MA based compatibilizers.

It can be concluded that improving the impact properties of the PP/PET blends is most successful with POE-g-MA, while PP-g-MA is better at improving the tensile and flexural properties. SEBS-based compatibilizers seem to have little or even a negative effect on the mechanical properties of the blends. In future research the complementary SEM images could provide more insight in the effectiveness of the different compatibilizers.

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REFERENCES

Asgari, M. & Masoomi, M., 2012. Thermal and impact study of PP/PET fibre composites compatibilized with Glycidyl Methacrylate and Maleic Anhydride. *Composites Part B: Engineering*, 43(3), pp.1164–1170.

Van Bruggen, E. et al., 2016. Influence of processing parameters and composition on the effective compatibilization of polypropylene–poly (ethylene terephthalate) blends. *International Polymer Processing*, 31(2), pp.179–187.

Champagne, M.F. et al., 1999. Reactive compatibilization of polypropylene/polyethylene terephthalate blends. *Polymer Engineering & Science*, 39(6), pp.976–984.

Chiu, H.-T. & Hsiao, Y.-K., 2006. Compatibilization of poly (ethylene terephthalate)/polypropylene blends with maleic anhydride grafted polyethylene-octene elastomer. *Journal of Polymer Research*, 13(2), pp.153–160.

Entezam, M. et al., 2012. Influence of interfacial activity and micelle formation on rheological behavior and microstructure of reactively compatibilized PP/PET blends. *Macromolecular Materials and Engineering*, 297(4), pp.312–328.

Evstatiev, M., Fakirov, S. & Friedrich, K., 2005. Manufacturing and characterization of microfibrillar reinforced composites from polymer blends. In *Polymer Composites*. Springer, pp. 149–167.

G'Sell, C., Bai, S.-L. & Hiver, J.-M., 2004. Polypropylene/polyamide 6/polyethylene–octene elastomer blends. Part 2: volume dilatation during plastic deformation under uniaxial tension. *Polymer*, 45(17), pp.5785–5792.

Heino, M. et al., 1997. Compatibilization of polyethylene terephthalate/polypropylene blends with styrene–ethylene/butylene–styrene (SEBS) block copolymers. *Journal of applied polymer science*, 65(2), pp.241–249.

Jayanarayanan, K., Thomas, S. & Joseph, K., 2015. Effect of compatibilizer on the morphology development, static and dynamic mechanical properties of polymer-polymer composites from LDPE and PET. *International Journal of Plastics Technology*, 19(1), pp.84–105.

Kuzmanović, M. et al., 2016. The effect of injection molding temperature on the morphology and mechanical properties of PP/PET blends and microfibrillar composites. *Polymers*, 8(10), p.355.

Moini Jazani, O. et al., 2015. Effective parameters on the phase morphology and mechanical properties of PP/PET/SEBS ternary polymer blends. *Journal of Particle Science & Technology*, 1(1), pp.39–48.

Pang, Y.X. et al., 2000. Effects of a compatibilizing agent on the morphology, interface and mechanical behaviour of polypropylene/poly (ethylene terephthalate) blends. *Polymer*, 41(1), pp.357–365.

Pek, W.K. & Ghosh, U.K., 2015. Effect of binary mixture of waste plastics on the thermal behavior of pyrolysis process. *Environmental Progress & Sustainable Energy*, 34(4), pp.1113–1119.

Ragaert, K., Delva, L. & Van Geem, K., 2017. Mechanical and chemical recycling of solid plastic waste. *Waste Management*.

Tanrattanakul, V. et al., 1997. Fracture mechanisms of poly (ethylene terephthalate) and blends with styrene-butadiene-styrene elastomers. *Journal of materials science*, 32(18), pp.4749–4758.

Wang, F. et al., 2016. Enhancement of fracture toughness, mechanical and thermal properties of rubber/epoxy composites by incorporation of graphene nanoplatelets. *Composites Part A: Applied Science and Manufacturing*, 87, pp.10–22.

Zhang, X. et al., 2009. The effect of interfacial adhesion on the impact strength of immiscible PP/PETG blends compatibilized with triblock copolymers. *Polymer*, 50(19), pp.4737–4744.

Zhu, Y. et al., 2015. Compatibilization of polypropylene/recycled polyethylene terephthalate blends with maleic anhydride grafted polypropylene in the presence of diallyl phthalate. *Journal of Polymer Research*, 22(3), p.35.